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Coprecipitation of Manganese with Calcium Carbonate

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The distribution behavior of manganese with calcium carbonate, calcite and aragonite was studied at 25°C. Precipitates of calcite and aragonite were made from calcium bicarbonate solution by the homogeneous precipitation method. Five point seven was obtained as the logalithmic distribution coefficient of manganese with calcite, and 0.058 was obtained as that of manganese with aragonite. The reason why the distribution coefficient of manganese with calcite is about one hundred times as large as that with aragonite is considered to be the distortion energy in the aragonite crystals which comes from the difference of free energy of ideal solid solution and that of real solid solution.

INTRODUCTION

A large quantity of calcium carbonate is precipitating in the marine water system with marine organisms such as marine bivalves, and this is much concerned with the distribution of trace elements in marine water system. As the fixation of trace elements is very important from points of the food chain and accumulation of metals, there are several investigations dealing with the coprecipitation of trace elements with calcium carbonate.[1~7]

Previously, the coprecipitation behavior of cadmium with calcium carbonates was investigated.[8,9] In the present paper, author is reporting the results of the distribution behavior of manganese with calcite and aragonite as a fundamental study of the connection between trace elements in marine water and those in shell and shellfish.

EXPERIMENTAL

Apparatus and Reagents

The radioactivity countings were made with a Metro NaI(Tl) (44.5 mm in dia., 50.8 mm in length) well-type scientillation counter, Model PbW-6, connected with a Metro single channel pulse height analyzer, Model SP-6F. Radioisotope, manganese-54 was supplied by New England Nuclear, Mass., U.S.A., as chloride in hydrochloric acid. The radiotracer was diluted with 0.05 N hydrochloric acid to make an appropriate solution (about 5 μCi/ml). A calcium bicarbonate solution was prepared by passing carbon dioxide into a calcium carbonate suspension for several hours, and filtering it. The filtrate was passed again with carbon dioxide for half an hour. A manganese solution was prepared from manganese metal by dissolving it in hydrochloric acid. A magnesium chloride solution to make aragonite crystals was prepared from reagent-grade chloride. Concentration of stock solution of magnesium chloride was 5 M.

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A thermostat waterbath was controlled at 25.0°C by a mechanical stirrer. Concentration of calcium was measured by atomic absorption spectrometry (Jarrell Ash, Model AA-1).

Procedure

By the gradual release of carbon dioxide gas from calcium bicarbonate solution, calcite precipitated in a 1.0 l Erlenmayer flask. The flask was sealed with a silicon rubber stopper fitted with a glass tube. The glass tube was opened to the air. By a similar method to calcite, aragonite precipitated from the calcium bicarbonate solution containing magnesium chloride. Precipitation speed was controlled by changing the diameter of the glass tube connected with the flask through a silicon rubber stopper and opened to air. In the case of aragonite run, precipitation speed controll was also made by ventilation of nitrogen gas in the flask. Nitrogen gas flow rate was 1.1 ml/min and 4.0 ml/min. One liter of the aqueous solution which contained 0.01 M of calcium bicarbonate solution, appropriate amounts of manganese, manganese-54, and magnesium chloride in the case of aragonite run, was taken in an Erlenmayer flask. Stirring by teflon coated bar, calcite and aragonite were precipitated from the solution in the flask supported in the water bath. Concentrations of calcium and manganese were measured by the following method. A supernatant solution was pipetted out every suitable interval of time, and precipitates were removed by a centrifuge. Concentration of manganese was calculated from radioactivity of the solution containing manganese-54 by the single channel scintillation counter. After countings, the solutions were diluted by one tenth, and 2 ml of the diluted solution, 2 ml of a buffer solution (pH=9.2), 2 ml of distilled water, 2 ml of 1% DDTC solution, and 5 ml of DIBK were taken in the separation funnel. After shaking the funnel, concentration of calcium in the aqueous solution was measured by atomic absorption spectrometry.

RESULTS AND DISCUSSION

As a crystal grows from a solution, micro components distribute between solid phase and liquid phase in two characteristic manners. One is called the homogeneous distribution law,[10,11] which holds good when the equilibrium between liquid phase and the inside of solid phase is achieved, and expressed as follows:

$$D=\frac{C_{Ca}\cdot M_{MnCO_3}}{C_{Mn}\cdot M_{CaCO_3}} \tag{1}$$

where C_{Ca} and C_{Mn} are the total concentrations of calcium and manganese ions in the solution. M_{CaCO_3} and M_{MnCO_3} are the mole fractions of calcium and manganese in the carbonate. The other is called the logarithmic distribution law, and expressed as follows:[12]

$$\lambda=\log\frac{C_{Mn,initial}}{C_{Mn,final}}/\log\frac{C_{Ca,initial}}{C_{Ca,final}} \tag{2}$$

The distribution of microcomponents depends on the manner of crystallization, and in the precipitates made by the homogeneous precipitation method, the system usually obeys the logarithmic distribution law. According to McIntire,[13] nonequilibrium logarithmic distribution coefficient, λ', is affected by the degree of supersaturation of

the solution. If the diffusion coefficients of micro- and macro-components are very nearly equal, λ', is expressed as follows:

$$\lambda' = \frac{\lambda S}{\lambda(S-1)+1} \tag{3}$$

where S is the degree of supersaturation of the solution. From the equation above, the nonequilibrium distribution coefficient is affected by S. Then, the distribution coefficient should be measured in different precipitation rate. Control of precipitation rate was made by changing the diameter of glass tubes from 2.5 mm to 10 mm to precipitate calcite, and from 5 mm to 20 mm to precipitate aragonite. In addition, the method for flowing nitrogen gas over the solution in the flask was also adopted to make aragonite precipitates. Precipitation rate is shown as $t_{1/2}$, which is the time required for fifty per cent precipitation of calcium.

Coprecipitation of Manganese with Calcite

Coprecipitation of manganese with calcite at various precipitation rates is shown in Fig. 1. Initial concentration of manganese was 5×10^{-6} M. The figure shows that the distribution behavior of manganese is scarcely affected by the precipitation rate in the range investigated.

The true distribution coefficient should be independent of the molar ratio between micro- and macro-components. The upper limit of the initial concentration of manganese is restricted by the solubility product of its carbonate, and the lower limit is restricted by absorption process on the calcite precipitates. In order to examine the molar ratio of Mn to Ca, calcite was precipitated changing the initial concentration of manganese from 5×10^{-8} to 5×10^{-4} M. The results are shown in Fig. 2. Distribution coefficients at the lower concentration are slightly larger because of the existence of absorption process.

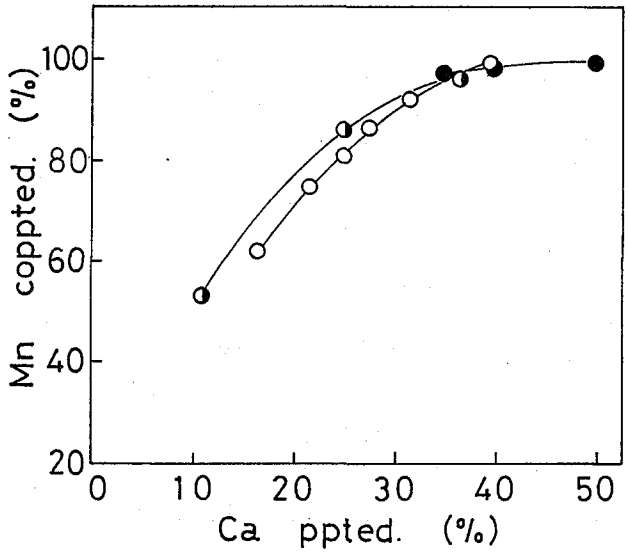

Fig. 1. Effect of precipitation rate of calcite.
●: $t_{1/2}$=0.5 days, ◑: $t_{1/2}$=1.5 days, ○: $t_{1/2}$=3 days, [Mn]=5×10^{-6} M.

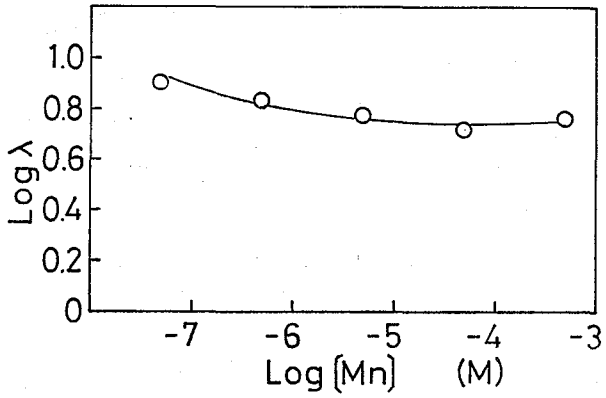

Fig. 2. Effect of concentration of manganese on the distribution coefficient in calcite system.

Distribution of Manganese with Aragonite

In order to make aragonite precipitates, it is necessary that magnesium chloride is added to the calcium bicarbonate solution. The precipitation rate of calcite became slower than that of calcite. Precipitation rate, $t_{1/2}$, was 6.5, 5, and 3 days when the diameter of glass tubes was 5, 10, and 20 mm, respectively. When the flow rate of nitrogen gas was 1.1, 4, and 14 ml/min, $t_{1/2}$ was 3, 1.7 days, and 1 day, respectively.

As the surfaces of precipitates of the first stage crystallization was very active, abnormal incorporation was often observed. As the plots of coprecipitation per centage of manganese versus precipitation percentage of calcium did not pass the zero point, distribution coefficients were calculated omitting the first absorption stage. Figure 3 shows the effect of the precipitation rate; the initial concentration of manganese is 5×10^{-6} M and concentration of magnesium chloride is 0.02 M. The results show that $t_{1/2}$ should be longer than 3 days.

The effect of the molar ratio between manganese and calcium in aragonite was examined ranging the initial concentration of manganese from 5×10^{-8} to 5×10^{-5} M, and the results were shown in Fig. 4. When the concentration of manganese was $5\times$

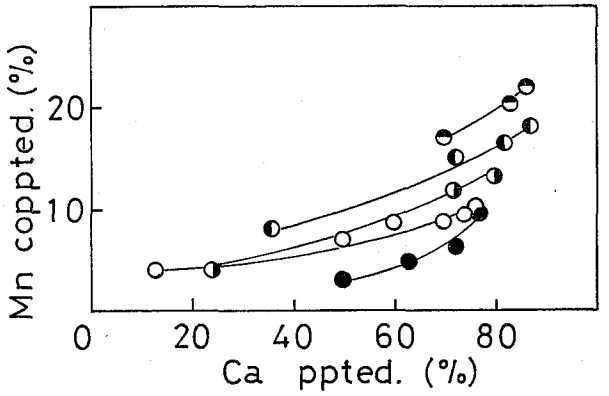

Fig. 3. Effect of precipitation rate of aragonite.
◑: $t_{1/2}$=3 days, ○: $t_{1/2}$=5 days, ◓: $t_{1/2}$=1 day (N_2 gas flow), ◐: $t_{1/2}$=1.7 days (N_2 gas flow), ●: $t_{1/2}$=3 days (N_2 gas flow), [Mn]=5×10^{-6} M, [$MgCl_2$]=0.02 M.

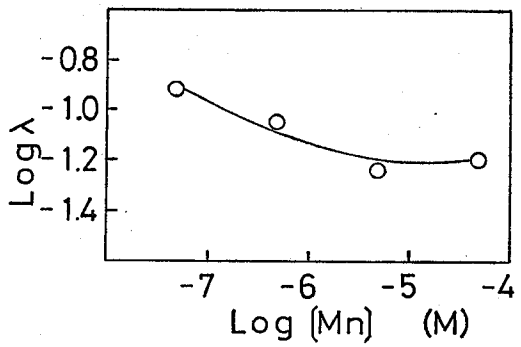

Fig. 4. Effect of concentration of manganese on the distribution coefficient in aragonite system.
$t_{1/2}$=3 days (N_2 gas flow), [$MgCl_2$]=0.02 M.

10^{-4} M, the coprecipitation of manganese much increased because of the precipitation of manganese carbonate.

As chloride ions scarcely react manganese and calcium ions, it is expected that the distribution of manganese will not be influenced by the concentration of magnesium chloride. As aragonite was precipitated from the solution containing more than 0.02 M of magnesium chloride, we examined the effect of magnesium chloride ranging the concentration from 0.02 to 0.08 M, and the results are shown in Fig. 5. From the results, we can say that the distribution coefficients are not effected by magnesium chloride within this concentration range.

Chlopin's distribution coefficient, D was given as a thermodynamic expression by Ratner[14] and Vaslow and Boyd[15] as follows:

$$D=\frac{K_{CaCO_3}}{K_{MnCO_3}}\cdot\left(\frac{\gamma_{Mn}}{\gamma_{Ca}}\right)\exp\left(\frac{-\Delta\mu}{RT}\right) \qquad (4)$$

where K_{CaCO_3} and K_{MnCO_3} denote the thermodynamic solubility product constants for $CaCO_3$ and $MnCO_3$, γ_{Ca} and γ_{Mn} stand for molar activity coefficients of calcium and manganese in the solution phase, and $\Delta\mu$, the excess free energy, is the partial molar free energy involved in transferring one mole of manganese ions from a large quantity of ideal solid solution to the real solid solution at the same mole fraction. Distribution

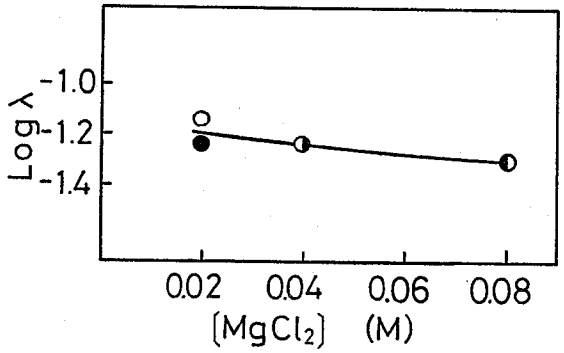

Fig. 5. Effect of concentration of magnesium chloride.
○: $t_{1/2}$=1.7 days, ●: $t_{1/2}$=3 days, ◑: $t_{1/2}$=2 days, ◐: $t_{1/2}$=2.4 days, [Mn]=5×10^{-6} M.

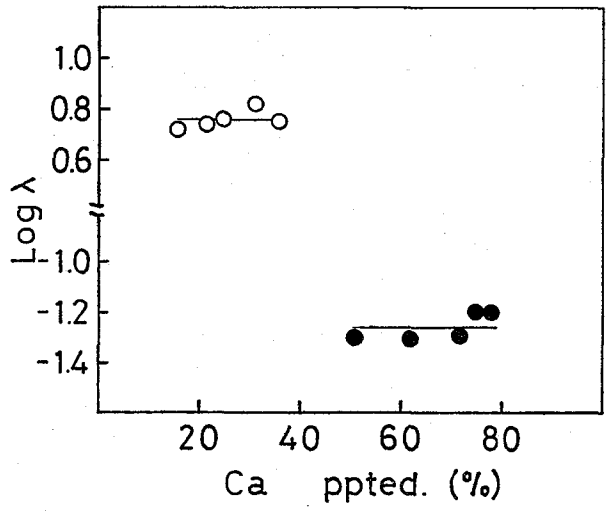

Fig. 6. Distribution coefficient of manganese with calcite and aragonite.
○: calcite, ●: aragonite, $[MgCl_2]=0.02$ M, $[Mn]=5\times10^{-6}$ M.

coefficient, D in Eq. 4, is composed of a product of three terms. If the solid solution is ideal, the distribution coefficient is expressed by the ratio of solubility products of micro- and macro-components because the second and the third terms become unity. Distribution coefficients of manganese with calcite and with aragonite are shown in Fig. 6 under typical conditions. The distribution coefficient of manganese with calcite is about one hundred times as large as that with aragonite. If the third term of Eq. 4 is negligible in the manganese-calcite system, the term becomes an important factor for the manganese-aragonite system. Namely, the excess free energy is an essential factor for the distribution of manganese with arganotie. This may be caused by the fact that manganese carbonate has only a calcite form and ion radius of calcium is 0.99 Å, but that of manganese is 0.80 Å.

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